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(54) PROPYLENIC RESIN COMPOSITION AND FILM OR SHEET

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## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a propylenic resin composition giving a propylenic film or sheet which is largely improved in heat seal strength.

SOLUTION: Peak top temperature ( $T_c$ ) in the maximum temperature of a crystallizing curve and a differential calorie ( $\Delta H_m$ ) of a melting curved measured using a differential scanning calorimeter(DSC) satisfy  $T_c \geq ((1/4) \cdot \Delta H_m + 90)$ , and further, a frequency ( $\omega$ ) and  $\Delta H_m$  in which a storage elastic modulus ( $G'$ ) and loss elastic modulus ( $G''$ ) in frequency dispersion measurement of  $\Delta H_m$  and melt viscoelasticity satisfy  $G' = G''$  fulfill  $\omega \leq ((1/10) \cdot \Delta H_m + 15)$ .

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 CLAIMS
 

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## [Claim(s)]

[Claim 1] The differential heating value ( $\Delta H_m$  (J/g)) in the peak top temperature ( $T_c$  (degree C)) and the melting curve by the side of the maximum temperature in the crystallization curve measured with the differential scan mold calorimeter (DSC) fills the following relational expression (1-1), and it is  $T_c \geq (1/4)$  and  $\Delta H_m + 90$ . ... (1-1)

And the propylene system resin constituent with which the frequency ( $\omega$  (rad/sec)) and  $\Delta H_m$  to which the storage modulus ( $G'$  (Pa)) and loss modulus ( $G''$  (Pa)) in frequency dispersion measurement of melting viscoelasticity become equal fill the following relational expression (2-1).

$\omega \leq (1/10)$  and  $\Delta H_m + 15$  ... (2-1)

[Claim 2] The propylene system resin constituent according to claim 1 which consists of propylene system [polymer I] 1-99 % of the weight which fills following (1) - (3), and crystalline propylene system polymer [II] 99-1 % of the weight.

(1) It is  $\Delta H_m \geq 6 \times (T_m - 140)$  with which  $T_m$  and amount of fusion endoergic  $\Delta H$  (J/g) fill the following relation when the melting point ( $T_m$  (degree C)) is not shown or  $T_m$  is shown in (3) DSC measurement whose amount of components (H25) eluted in the hexane which is (2) 25 degree C whose amount of components (W25) eluted below 25 degrees C in temperature programmed chromatography is 20 - 100 % of the weight is 0 - 80 % of the weight.

[Claim 3] The propylene system resin constituent according to claim 1 which consists of propylene [homopolymer a] 1-99 % of the weight which fills following (1) - (3), and crystalline propylene system polymer [II] 99-1 % of the weight.

(1) [Claim 4] whose amount of components (W25) in which a meso pentad molar fraction (mmmm) is eluted below 25 degrees C in the  $[rrrr/(1-mmmm)] \leq 0.1$  (3) temperature programmed chromatography with which 20-60-mol (2) raceme-pentad molar fraction (rrrr) it is [ molar fraction ] %, and (1-mmmm) fill the following relation is 20 - 100 % of the weight The propylene system resin constituent according to claim 2 or 3 with which the propylene system polymer [I] in claim 2 or the propylene homopolymer [a] in claim 3 fills following (1) and/or (2).

(1) a gel permeation chromatograph (GPC) — limiting viscosity measured at 135 degrees C among (2) tetralin solvent whose molecular weight distribution ( $M_w/M_n$ ) measured by law are four or less [eta] [Claim 5] which is 0.5-15.0 deciliters/g The propylene system resin constituent according to claim 2 to 4 which the propylene system polymer [I] in claim 2 or the propylene homopolymer [a] in claim 3 does not show the melting point ( $T_m$  (degree C)) in DSC measurement.

[Claim 6] The film or sheet which has the layer which consists of a propylene system resin constituent according to claim 1 to 5.

[Claim 7] JIS The film according to claim 6 or sheet whose Hayes of the film measured according to K7105 or a sheet is 10% or less.

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TECHNICAL FIELD

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[Field of the Invention] This invention relates to the film and sheet which consist of the new propylene system resin constituent and new it which give the film whose heat-sealing reinforcement was excellent in flexibility and transparency in more detail, and improved sharply, and a sheet about the film and sheet which consist of a propylene system resin constituent and it. Moreover, the propylene system resin constituent of this invention is suitably used also as much more constituent of the laminated film laminated and co-extruded and a sheet at least.

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EFFECT OF THE INVENTION

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[Effect of the Invention] The propylene system resin constituent of this invention gives the propylene system film or sheet whose heat-sealing reinforcement heat-sealing temperature was moderately low-temperature-ized, and improved sharply. Moreover, the film whose heat-sealing reinforcement was rich in flexibility, and was excellent also in transparency and thermal resistance, and improved sharply with the propylene system resin constituent of this invention, and a sheet are obtained, and it is suitably used as an alternative of elasticity vinyl chloride system resin.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] The purpose of this invention is offering the new propylene system resin constituent which gives the propylene system film or sheet whose heat-sealing reinforcement's heat-sealing temperature's was moderately low-temperature-ized, and improved sharply, the film which comes to reach, and a sheet. Furthermore, other purposes of this invention are offering the new propylene system resin constituent which can serve as an alternative of the elasticity vinyl chloride system resin whose heat-sealing reinforcement's was rich in flexibility, and was excellent also in transparency and thermal resistance, and improved sharply, the film which comes to reach, and a sheet.

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## EXAMPLE

[Example] Although this invention is explained still more concretely below based on an example, this invention is not restricted at all by these examples. First, the evaluation approach of the resin property in this invention and film quality is explained.

"The evaluation approach of a resin property"

(1) [eta] Measurement In 135 degrees C, it measured using the VMR-053 mold automatic viscometer of RIGOSHA among the tetralin solvent.

(2) It measured by the approach indicated in the measurement specification text of a pentad molar fraction and an abnormality insertion molar fraction. That is, based on the approach proposed by ray Zhang Berry (A. Zambelli) etc. by "Macromolecules, 6,925 (1973)", the meso pen DADD0 molar fraction (mmmm molar fraction) and the raceme pentad molar fraction (rrrr molar fraction) measured the signal of the methyl group of <sup>13</sup>C nuclear-magnetic-resonance spectrum, and asked for the isotactic molar fraction and atactic molar fraction in a pentad unit in a polypropylene chain by the following formula.

<formula>  $M = m/S \times 100$   $R = \gamma/S \times 100$   $S = P*****P*****$  signal on-the-strength  $P*****: 19.8 - 22.5 \text{ ppm}$   $P*****$ : of the side-chain methyl carbon atom of a PalphagammaS: all propylene unit --  $\gamma: 17.5 - 17.1 \text{ ppm}$  [ of  $18.0 - 17.5 \text{ ppm}$   $P \alpha$  ]  $\gamma$ : raceme pentad chain: --  $20.7 - 20.3 \text{ ppm}$  meso pentad chain:  $21.7 - 22.5 \text{ ppm}$  -- again -- ( -- m-2 and 1), (2 r- one) And (1 3) attribution of the peak of a <sup>13</sup>C-NMR spectrum was determined based on Grassi's and others report (Macromolucules, 21, and p.617), and (1988) Busico's and others report (Macromolucules, 27, p.7538 (1994)), and each insertion content was computed from the integrated intensity of each peak. (m-2 and 1) is Palpha and gammathreo which appear near [ to the integrated intensity in all methyl carbon fields ]  $17.2 \text{ ppm}$ . The belonging ratio of the integrated intensity of a peak was computed as meso -2 and 1 insertion content (%). (r-2 and 1) is Palpha and gammathreo which appear near [ to the integrated intensity in all methyl carbon fields ]  $15.0 \text{ ppm}$ . The belonging ratio of the integrated intensity of a peak was computed as racemic -2 and 1 insertion content (%). T to which (1, 3) appear near [ to the integrated intensity in all methine carbon fields ]  $31.0 \text{ ppm}$  -- the ratio of the integrated intensity of a peak which belongs to beta and gamma10 was computed as 1 and 3 insertion content (%). When the peak which should belong to meso -2, 1 insertion, racemic -2, 1 insertion or 1, and 3 insertion may be unable to identify by hiding in a noise etc. in addition, under [ all / 0 / each different-species joint content (2 m- 1) or (2 r- 1) (1 3) ].

[0090] Measurement of <sup>13</sup>C nuclear-magnetic-resonance spectrum was performed on following equipment and following conditions.

equipment: -- JNM-EXby JEOL Co., Ltd. 400 mold <sup>13</sup>C-NMR equipment approach: -- proton perfect decoupling method concentration: -- 220mg [ /ml ] solvent: -- 90:10 (capacity factor) mixed-solvent temperature [ of 1,2,4-trichlorobenzene and heavy benzene ]: -- 130-degree-C pulse width: -- 45-degree pulse repetition-time: -- 4-second addition: -- measurement Mw/Mn of 10000 times (3) molecular weight distribution (Mw/Mn) was measured by the approach indicated in the specification text. That is, Mw/Mn is the value computed by the GPC method from the weight average molecular weight Mw and number average molecular weight Mn of polyethylene conversion which were measured on following equipment and following conditions.





chromatography Product made from FOXBORO MIRAN 1A CVP Method bulb of ten : Made in Barco Electric bulb Loop formation : Made in Barco 500 microliter loop-formation (c) Measuring condition Solvent : o-dichlorobenzene Sample concentration : 7.5g/l. Injection rate : 500 microliter Pump flow rate : A part for 2.0ml/ Detection wave number : 3.41 micrometers Column packing material : Chromosorb P (30-60 meshes)

Column temperature distribution : The amount of components eluted in less than \*\*0.2-degree-C (8) hexane (H25)

H25 was measured and calculated in the following Measuring condition.

[0092]

Sample :0.1-5g sample configuration: The shape of powder (what was pelletized grinds and powder-izes and uses)

solvent : -- hexane elution condition: -- it computes by the formula below calculation approach: of a standing elution volume more than for 25 degrees C and three days.

[0093]

$H25 = [(W0 - W1) / W0] \times 100 (\%)$

All the films that carried out "appraisal method of film quality" film production are (1) heat-sealing temperature and the heat-sealing reinforcement JIS which performed annealing treatment of 24 hours at the temperature of 40 degrees C, and measured further under the temperature same after [ 16 hours or more ] carrying out conditioning, and humidity conditions at the temperature of 23\*\*2 degrees C, and 50\*\*10% of humidity. It measured based on Z-1707. After carrying out the seal on condition that the following with the heat-sealing bar specifically proofread by the surface pyrometer and leaving it at a room temperature one whole day and night, peel strength (heat-sealing reinforcement) was measured by the T mold exfoliating method which set the exfoliation rate to 200mm / min at the room temperature. Heat-sealing temperature was defined as the temperature from which peel strength is set to 300g/15mm, and was searched for by count from the seal temperature-peel strength curve.

seal condition sealing-surface: -- a metal roll side / metal roll side sealing-surface product: -- 15x10mm seal pressure: -- 2.0kg / cm2 seal time amount: -- 1-second seal temperature: -- heat-sealing temperature can be interpolated -- as -- several point (2) transparency (Hayes) JIS (3) modulus of elasticity in tension JIS measured according to K7105 crosshead rate: measured on condition that the following by the tension test based on K7127 -- 500mm / min load cell: -- 10kg measurement direction: -- the direction (MD) of a machine

(4) In the rotation mold rheometer by the frequency dispersion measurement LEO metrics company of melting viscoelasticity, frequency dispersion measurement of melting viscoelasticity was performed using the cone plate (the diameter of 25.0mm, 0.10 radians of cone angle types) on the temperature of 175 degrees C, and the conditions of 20% of initial strains. It is complex-modulus  $G^*$  (iomega) at the time of a frequency (omega (rad/sec)) Stress sigma\* Strain gamma\* When it describes, it is  $G^* = (i\omega) \sigma^* / \gamma^* = G'(\omega) + iG''(\omega)$ . It becomes.

However, i is an imaginary unit.

[Example 1]

(1) Preparation of a catalyst (dimethyl silylene) 2(3-n-butyl indenyl) 2 It is 2 (indene (2 (1, 2'-dimethyl silylene), 1'-dimethyl silylene)) to the synthetic SHURENKU bottle of zirconium dichloride. 0.83g (2.4mmol) and ether 50mL are put in. - Stir at a room temperature for 12 hours after cooling at 78 degrees C and adding n-BuLi (hexane solution 1.6M) 3.1 mLs (5.0mmol). It is obtained 1.1g (2.3mmol) by washing the solid-state which might be distilled off in the solvent by hexane 20mL, using lithium salt as an ether adduct. This lithium salt is dissolved in THF50mL, and it cools at -78 degrees C. bromination -- n-butyl 0.57mL (5.3mmol) is dropped slowly, and it stirs at a room temperature for 12 hours. After distilling off a solvent and extracting by hexane 50mL, a solvent is removed, and it is 2 (3(2 (1, 2'-dimethyl silylene), 1'-dimethyl silylene)-n-butyl indene). 0.81g (1.77mmol) was obtained. (74% of yield)

Next, 2 obtained above by the SHURENKU bottle under the nitrogen air current (3(2 (1, 2'-dimethyl silylene), 1'-dimethyl silylene)-n-butyl indene) 0.81g (1.77mmol) and ether 100mL are put in. - Stir at a room temperature for 12 hours after cooling at 78 degrees C and adding n-BuLi (hexane solution 1.54M) 2.7 mLs (4.15mmol). It was obtained 0.28g (1.43mmol) by distilling

off a solvent and washing the obtained solid-state by the hexane, having used lithium salt as the ether adduct.

[0094] The lithium salt obtained above under the nitrogen air current is dissolved in toluene 50mL. - The toluene (50mL) suspension of 0.33g of zirconium tetrachlorides which cooled at 78 degrees C and were beforehand cooled at -78 degrees C here (1.42mmol) is dropped. It stirs at a room temperature after dropping for 6 hours. It filters after that and the solvent of a filtrate is distilled off. It is 2 (3(2 (1, 2'-dimethyl silylene), 1'-dimethyl silylene)-n-butyl indenyl) by recrystallizing from dichloromethane. 0.2g (0.32mmol) of zirconium dichloride was obtained. (22% of yield)

1 result of measurement by H-NMR (90MHz and CDCl<sub>3</sub>): delta 0. -- it was 88, 0.99 (12H, dimethyl silylene), 0.7-1.0, 1.1-1.5 (18H, n-Bu), and 7.0-7.6 (8H, benzene ring proton).

(2) the autoclave made from stainless steel of 10l. of polymerization content volume of a propylene -- 6l. of heptanes, and triisobutylaluminum -- 2 (3(2 (1, 2'-dimethyl silylene), 1'-dimethyl silylene)-n-butyl indenyl) further obtained with the above with methyl aluminoxane (made in Albemarle) 5 millimol 6 millimol The catalyst component which carried out preliminary contact of the zirconium dichloride 5 micromole for 5 minutes in toluene was supplied. Here, after introducing G 0.5kg/cm<sup>2</sup> of hydrogen, the propylene was supplied with the pressure governor so that 8.0kg/cm<sup>2</sup> of propylene gas might be introduced to G with total pressure and the polymerization medium-voltage force might become fixed. The propylene homopolymer (B-1) was obtained by taking out contents and drying under reduced pressure at the polymerization temperature of 50 degrees C, after performing a polymerization for 30 minutes.

(3) The following additives were prescribed to the polypropylene homopolymer (B-1) obtained by combination and the kneading above, it extruded and corned with the single screw extruder (made in the Tsukada tree machine factory: 35 to TLC20 mold), and the pellet was obtained. (Additive formula)

phenolic antioxidant: -- the product made from tiba speciality KEMIKARUZU -- IRUGA NOx 10101000ppm Lynn system anti-oxidant: -- P-EPQ500ppm neutralizer made from tiba speciality KEMIKARUZU: -- calcium stearate: -- 500 ppm neutralizer: -- the above-mentioned approach as a manufacture propylene system polymer [I] of a DHT-4A:500 ppm(4) resin constituent Idemitsu polypropylene F-704NP could be supplied to 85 weight sections blender as the manufactured propylene system polymer [a-1] 15 weight section and a crystalline propylene system polymer [II], it mixed, and piston granulation was further carried out with the single screw extruder (made in the Tsukada tree machine factory: 35 to TLC20 mold).

(5) The evaluation approach in which (6) resin property fabricated on the conditions of the resin temperature [ in / using the pellet of the propylene system resin constituent which carried out in this way and was obtained to a Tsukada tree machine factory 20mmphi extruder / a T-die outlet ] of 190 degrees C, the chilled roll temperature of 30 degrees C, and 6m in film production taking over rate / min of a film on the film of 50 micrometers of thickness, and physical properties carried out the evaluation above estimated. The obtained result is shown in Table 1 and 2.

[Example 2] The propylene system polymer [a-1] 30 weight section and Idemitsu polypropylene F-704NP were performed like the example 1 except [ all ] having changed the blend ratio into 70 weight sections. The obtained result is shown in Table 2.

[Example 3] The propylene system polymer [a-1] 60 weight section and Idemitsu polypropylene F-704NP were performed like the example 1 except [ all ] having changed the blend ratio into 40 weight sections. The obtained result is shown in Table 2.

[Example 1 of a comparison] It carried out like the example 1 except [ all ] having used the ethylene-propylene copolymer rubber (grade name : EP913Y) of Japan Synthetic Rubber Co., Ltd. instead of the propylene system polymer [a-1]. The obtained result is shown in Table 2.

[Example 2 of a comparison] It carried out like the example 2 except [ all ] having used the ethylene-propylene copolymer rubber (grade name : EP913Y) of Japan Synthetic Rubber Co., Ltd. instead of the propylene system polymer [a-1]. The obtained result is shown in Table 2.

[Example 3 of a comparison] It carried out like the example 3 except [ all ] having used the ethylene-propylene copolymer rubber (grade name : EP913Y) of Japan Synthetic Rubber Co.,

Ltd. instead of the propylene system polymer [a-1]. The obtained result is shown in Table 2.

[Example 4 of a comparison] A propylene system polymer [1] was not blended but it carried out like the example 1 except [ all ] having used Idemitsu polypropylene F-704NP independently. The obtained result is shown in Table 2.

[Example 5 of a comparison] A propylene system polymer [1] was not blended but it carried out like the example 1 except [ all ] having used Idemitsu polypropylene F-454NP independently. The obtained result is shown in Table 2.

[Example 6 of a comparison] A propylene system polymer [1] is not blended but he is Idemitsu TPO. It carried out like the example 1 except [ all ] having used E2900 independently. The obtained result is shown in Table 2.

[0095]

[Table 1]

表 1

プロレン系重合体 (1)	(a-1)
W 2 5 重量%	93
H 2 5 重量%	17
$\Delta H$ J/mol	n. d.
$6 \times (T_m - 140)$	—
mmmm分率 %	41
rrrr/(1-mmmm) %	4
2.1 挿入分率 %	0
1.3 挿入分率 %	0
Mw/Mn	2.4
$[\eta]$ dl/g	2.5
Tm °C	n. d.
Tc °C	n. d.
引張弾性率 MPa	31

n. d. : 観測されない

[0096]

[Table 2]

表 2

		実施例-1	実施例-2	実施例-3	比較例-1	比較例-2	比較例-3	比較例-4	比較例-5	比較例-6
配合割合	プロピレン系重合体(I) (重量%)	(a-1) 15	(a-1) 30	(a-1) 60	EP913Y 15	EP813Y 30	EP913Y 60	— 0	— 0	— 0
	結晶性プロピレン系重合体(II) (重量%)	F-704NP 85	F-704NP 70	F-704NP 40	F-704NP 85	F-704NP 70	F-704NP 40	F-704NP 100	F-454NP 100	E2900 100
樹脂特性	$\Delta H_m$ (J/g)	88	73	41	83	62	38	100	87	72
	$T_c$ (°C)	115.2	112.3	106.1	111.9	111.9	112.2	112.4	113.8	106.4
	$(1/4)\Delta H_m + 90$ (rad/sec)	112.1	108.3	100.3	110.7	105.5	99.6	115.1	111.7	108.1
	$\omega(G' = G'')$ (rad/sec)	21	16	12	47	70	100<	25	25	18
	$(1/10)\Delta H_m + 15$	24	22	19	23	21	19	25	24	22
物理特性	ヘイズ (%)	1.8	1.8	3.6	2.1	11.0	5.5	1.6	61.0	13.5
	引張強度MD (MPa)	741	518	166	873	612	343	1040	856	486
	ヒートシール温度 (°C)	152	144	130	145	138	129	155	154	158
	ヒートシール強度 (gf/15mm)									
	シール条件温度115°C						63			
	シール条件温度120°C						116			
	シール条件温度125°C						199			
	シール条件温度130°C						322			
	シール条件温度135°C			269		298	293			
	シール条件温度140°C		111	1031	209	302	344			
	シール条件温度145°C		333	1289	303	306	372			
	シール条件温度150°C	137	695	1505	455	329	339	155	124	88
	シール条件温度155°C	494	1359	1699	971	389	381	256	345	99
	シール条件温度160°C	1449	2920	2020	916	486	461	1052	600	443
	シール条件温度165°C	3900	3087	2147	939	411	444	2484	1682	1553
	シール条件温度170°C	3453	3353				483	3105	2646	3641
	シール条件温度175°C	3662					525	3690		3479

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